

## CHARACTERIZATION OF SOLIDS FROM COAL/RESID COPROCESSING

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### ABSTRACT

Solids formed from coprocessing of 10% coal/90% resid were characterized by solvent extraction, elemental analyses,  $C^{13}/C^{12}$  isotope ratio, ESR, and GPC techniques. The total solids obtained from filtration contained at least 60% adsorbed petroleum-derived material (oil, resin, asphaltene). The THF insolubles in the product contained high oxygen, low vanadium and a higher level of polyaromatic radicals than the soluble fraction, indicating that these insolubles were largely coal-derived material. However, the fraction of the solid product that could be dissolved in either THF or pyridine was mostly petroleum-derived.

### INTRODUCTION

The background technology of the coprocessing of coal/petroleum resids has been reviewed by Oelert (1), and additional citations have been discussed in our companion paper (2) being presented at this conference. In summary, such coprocessing is done with the goals of providing the addition of a low cost feedstock, coal; improving unit operability by a reduction in petroleum-derived coke solids; enhancing metals and heteroatom removal; and reducing hydrogen requirements relative to direct coal liquefaction.

Our other paper reported on the coprocessing of 10% Illinois No. 6 coal with 90% resid with decanted oil (DCO) over equilibrium hydrotreating catalyst in a flow unit at 780°F. The addition of coal considerably increased the yield of solids obtained from a Shell hot filtration test, SHFT (2), as seen in Table I.

Normally, in resid hydroprocessing, SHFT solids are free of asphaltenes. The petroleum asphaltene concentration in the product of resid hydroprocessing is calculated as the difference between hexane insolubles and SHFT solids. For the resid/DCO experiment shown in Table I, the asphaltene level is 8.2 wt%. The asphaltene content of the coal/resid/DCO run in Table I calculated in the same manner is lower, 5.2 wt%. If the same levels of petroleum-derived asphaltenes are being formed in both cases, a reasonable assumption (although not certain), the SHFT solids obtained from coal/resid coprocessing must include some petroleum asphaltenes. Therefore, the use of SHFT solids to define asphaltene yield is not valid for the coal/resid case. Moreover, material balance analysis indicated that in addition to asphaltenes, a considerable amount of oil and resin was adsorbed by the unconverted coal.

The objective of this study was to characterize the solids from the coprocessing of coal and resid/DCO. This included verifying the presence of adsorbed petroleum-derived material in the solids; determining the relative distribution of coal-derived and resid-derived fractions; and characterizing the adsorbed petroleum-derived material.

### EXPERIMENTAL

Reaction Conditions. The coprocessing of 10% Illinois No. 6 with 90% resid with DCO was conducted in an upflow high-pressure unit which contains two 1-liter Autoclave reactors in series. Catalyst baskets, each filled with 60 cc of equilibrium hydrotreating catalyst, were placed in both reactors. To prevent elutriation, the catalyst was covered with 10 cc of 3 mm glass balls and 1/4 inch

of glass wool. The experiment was conducted at reactor temperatures of 780°F, average feed rate of 206 g/hr and 2500 psig H<sub>2</sub> at 7700 SCFB.

**Product Filtration.** In addition to the standard SHFT solids determination (2), a modified procedure was used as follows. A composite product was made by blending portions of the daily product samples collected over the 180 hours of coprocessing. This composite product was filtered, the solids were washed with a mixture of 10% toluene and 90% hexane, and then dried in a vacuum oven at 110°C for 16 hours.

**Solubility Fractionation.** The solids recovered from the above filtration of composite product were sequentially extracted with toluene followed by THF to separate the different solubility fractions. The schematic of the extraction procedure is shown in Figure 1.

**Product Analysis.** The extracted solubility fractions were analyzed for elemental composition (C,H,N,S,O), metals content (Ni,V) using inductively coupled plasma spectroscopy (ICP), molecular weight distribution using gel permeation chromatography (GPC), and relative levels of polyaromatic radicals and vanadium concentrations using electron spin resonance spectroscopy (ESR). In addition to conventional hexane precipitation, the extracts were separated into oils, resins, asphaltenes and preasphaltenes using a chromatographic technique (3). Oils were eluted from silica gel by hexane; resins were eluted from silica gel by diethyl ether/ethanol (10/1 volume ratio). Asphaltenes and preasphaltenes were insolubles that did not get passed over the silica gel; asphaltenes were toluene soluble (TS), and preasphaltenes were THF soluble and toluene insoluble (THFS/TI). Preasphaltene extraction was also done with pyridine in one case to provide a comparison with THF extraction results.

## RESULTS AND DISCUSSION

A mixture of 90% resid and 10% DCO was hydroprocessed for 120 hours, followed by a run period of 180 hours with an added 10% coal. The THF insolubles during the resid/DCO period averaged 0.6 wt%. This value was 3.3 wt% during the coal/resid/DCO period. Therefore, the level of coal conversion to THF solubles was about 80%, assuming no additional THF insolubles were formed from the petroleum-derived feeds during the period of coal addition. This value is lower than the coal conversion results reported by Wilsonville using a similar coal and a coal-derived recycle solvent (4), rather than petroleum liquids. However, due to the low coal feed concentration and the accuracy of the THF insolubles determination, it is not possible to ascertain whether this low conversion is due to solvent effectiveness or to solids being formed from the petroleum feeds.

The SHFT solids during the resid/DCO period averaged 2.3 wt%. This value was 9.6 wt% during the coal/resid/DCO period. The SHFT solids from resid/DCO and coal/resid/DCO hydroprocessing were analyzed for C<sup>13</sup>/C<sup>12</sup> concentration ratios using mass spectrometry to determine the relative amounts of coal-derived (or resid-derived) carbon in the SHFT solids. The analyses were performed by Global Geochemistry Corporation in Canoga Park, CA and it was assumed that there was no selective fractionation of the isotopes. The analysis on the SHFT solids indicated that only 28.0% of the solids was coal-derived. Therefore, 6.9% (absolute) was derived from the petroleum fractions, substantially more than the insolubles observed formed without coal present.

The feed coal and the modified SHFT solids from the coal/resid/DCO coprocessing were sequentially extracted with toluene followed by THF to separate different solubility fractions. Table II shows the yields of the solubility fractions from these solids and from the feed coal. The analysis of each of the soluble fractions from the modified SHFT solids for group type is shown in Table III; also shown is the analysis of the resid feed. The relative levels of radical concentrations and vanadium content (paramagnetic V<sup>0+2</sup>) in selected group types in

each of the solubility fractions were determined from ESR and are shown in Table IV. The elemental composition and metals content (as determined by ICP) of the solubility fractions from the modified SHFT solids are shown in Table V (also shown are the compositions for the coprocessing feed and for the product filtrate). The molecular weight distributions of the toluene soluble fraction (TS) of the coal feed, resid/DCO feed, TS of the modified SHFT solids, and preasphaltenes (THFS/TI) of the modified SHFT solids are shown in Figures 2a,b,c and d, respectively.

Unconverted Coal and THF Insolubles. As shown in Table II, the solids recovered from the filtration of composite product with hexane/toluene (90/10) wash and then THF contained 30 wt% THF insolubles (THFI). If the hexane/toluene wash did not affect the results of the subsequent THF extraction, the THF insolubles (as determined from this sequential extraction) is 2.9 wt% of the product. This value is within the experimental error of 3.3 wt% THF insolubles measured experimentally for the total coal/resid/DCO coprocessing product. Of the 3.3 wt%, 0.6 wt% is resid-derived so that the coal-derived THF insolubles is 2.7 wt%. This value is the same as the 2.7 wt% coal-derived solids inferred from the  $C^{13}/C^{12}$  isotope ratio analysis of the SHFT solids.

The high oxygen (Table V) and low vanadium content (Table IV) of the insolubles (THFI fraction) confirm that this is largely coal-derived material. Moreover, these insolubles contain a higher level of free radicals (Table IV) than the asphaltenes in the THF solubles material.

Analysis of the THF Soluble Fractions. The materials retained in the modified SHFT solids were primarily oils and resins, as shown in Table III. The THF solubles of the modified SHFT solids from the coal/resid/DCO run consisted of the toluene solubles and the preasphaltenes; it contained 36 wt% oils, 43% resins and only 21% asphaltenes+preasphaltenes (Table III). The recovered toluene soluble fraction contained 36% oils, 49% resins, and 10% asphaltenes; the remainder of this fraction was made up of preasphaltenes that formed as a result of the extraction and recovery process. The preasphaltene fraction was only about 8% of the modified SHFT solids.

The toluene soluble fraction of these modified SHFT solids was primarily petroleum-derived while the preasphaltenes were a mixture of petroleum- and coal-derived material. The low oxygen content (Table V) and molecular weight distribution (Figure 2b vs. Figure 2c) of the TS confirm that this material is mostly petroleum-derived. In addition, this toluene soluble material had an oil fraction which was very low in radical level (Table IV).

The preasphaltenes retained in the modified SHFT solids definitely had a coal component, as indicated by a high oxygen content (Table V) and the peak in the molecular weight distribution of an estimated value of 250 (Figure 2a vs. Figure 2d). Moreover, the resin fraction of these preasphaltenes contained more radicals than the resin fraction of the TS material (Table IV). These preasphaltenes also had a petroleum contribution, as indicated by its high metals content (Table V). The resin fraction of these preasphaltenes contained six times more vanadium (150 ppm) than the resin fraction of the toluene soluble material (25 ppm). Based on oxygen content, it is estimated that about 24% of the preasphaltenes was coal-derived.

The distribution of free radicals (of polyaromatic nature) among the group types (Table IV) confirms the above observations. Specifically, the free radical level in the asphaltenes is 68% that of the preasphaltenes in the modified SHFT solids. This would be expected if the level of coal-derived material was greater in the preasphaltenes. As a further test, pyridine extraction of the solids was carried out to obtain a pyridine soluble fraction. Pyridine as a more polar solvent extracted twice the level of free radicals than THF; this confirmed that part of the preasphaltenes was coal-derived. The pyridine-extracted preasphaltenes also

contained 20% more vanadium than the THF-extracted preasphaltenes, confirming the petroleum origin of the preasphaltenes.

The characteristics of the toluene soluble material extracted from the modified SHFT solids is shown in Table IV, along with those of the product filtrate and the coprocessing feed. This adsorbed petroleum-derived material had intermediate levels of sulfur, nitrogen and oxygen when compared to the product filtrate and the feed. Metal content was about the same as that of the filtrate and the H/C ratio was comparable to that of the feed. Therefore, this material, 21% of which is 1000°F, is possible additional liquid yield. There is a potential that some of the retained oils and part of the resins could be recovered in a vacuum tower during normal refinery processing.

#### SUMMARY AND CONCLUSIONS

The THF insolubles and the SHFT solids formed from the coprocessing of 10% Illinois No. 6 coal with a 90/10 resid/DCO feed at 780°F were characterized by solvent extraction,  $C^{13}/C^{12}$  isotope ratio, elemental analysis, ESR and GPC. The THF insolubles in these solids contained high oxygen, low vanadium, and a higher level of free radicals than the soluble fraction, indicating that these insolubles were largely coal and coal-derived material. In the characterization of SHFT solids, we found that material containing 36% oils, 43% resins, and 21% asphaltenes and preasphaltenes were retained. The toluene soluble fraction of the SHFT solids was petroleum-derived; and the preasphaltenes were of both coal and petroleum origins. The toluene soluble fraction of the SHFT solids had an intermediate quality between that of the feed and the product filtrate. This represents possible additional liquid yield.

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TABLE I. SOLIDS FROM HYDROPROCESSING AT 780 °F

<u>FEED</u>	<u>YIELD, wt% of feed</u>	
	<u>RESID/DCO</u>	<u>COAL/RESID/DCO</u>
THF Insolubles	0.6	3.3
Hexane Insolubles	10.5	14.8
SHFT Solids	2.3	9.6
Coal-derived SHFT Solids <sup>1</sup>	0.0	2.7

<sup>1</sup> C<sup>13</sup>/C<sup>12</sup> isotope analysis on SHFT solids indicated  
28.0±5.8% of the solids was coal-derived.

TABLE II. YIELDS OF SOLUBILITY FRACTIONS

<u>FRACTION</u>	<u>EXTRACTION YIELD, wt%</u>	
	<u>MODIFIED SHFT SOLIDS<sup>1</sup></u>	<u>ILLINOIS NO. 6 (MF BASIS)<sup>2</sup></u>
Toluene Solubles	62.5	0.6
Preasphaltenes (THF Soluble/ Toluene Insoluble)	7.6	1.8
THF Insolubles (THFI)	29.9	97.6 <sup>3</sup>

<sup>1</sup> 9.6 wt% of coprocessing feed (assuming hexane/toluene wash  
modification to the SHFT test had no effect)

<sup>2</sup> Coal moisture content of 7.1 wt%; coal ash content of 11.5  
wt% MF coal.

<sup>3</sup> THF extraction on coal gave 98.0 wt% MF coal.

TABLE III. GROUP TYPE ANALYSIS OF RESID FEED  
AND LIQUIDS FROM EXTRACTION OF MODIFIED SHFT SOLIDS

<u>FRACTION</u>	<u>DISTRIBUTION, wt% of fraction</u>				
	<u>OIL</u>	<u>RESIN</u>	<u>ASPHALTENE</u>	<u>PRE- ASPHALTENE</u>	<u>LOSSES</u>
Toluene Soluble	35.7	48.6	9.9	3.3	2.5
THF Soluble	36.0	43.1	10.5	10.4	0.0
Resid Feed	8.6	68.1	20.1	3.2	0.0

TABLE IV. RESULTS OF ESR ANALYSIS ON GROUP TYPES EXTRACTED FROM THE MODIFIED SHFT SOLIDS

	Relative Radical Concentration	Vanadium (ppm)
Toluene Soluble Oil	1	<0.1
Toluene Soluble Resin	500	25
Preasphaltene Resin	615	150
	Relative Radical Concentration	Vanadium (ppm)
Asphaltenes	1	680
Preasphaltenes:		
Pyridine-extracted	2.8	940
THF-extracted	1.5	785
THF Insolubles	1.6	230

TABLE V. FEED AND PRODUCT COMPOSITIONS

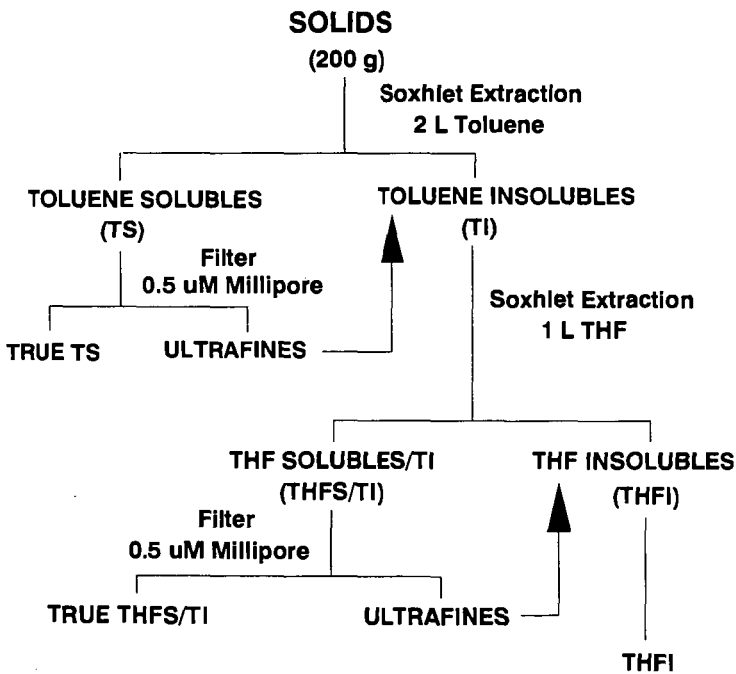
	ELEMENTAL COMPOSITION, wt%					ppm	ppm	(H/C)
	C	H	N	O	S	N1	V	
Coal/Resid/DCO Feed	84.47	9.55	0.52	1.68	4.35	45	177	1.36
Modified SHFT Filtrate	86.24	10.55	0.44	1.11	2.35	24	73	1.47
Modified SHFT Solids:								
Toluene Soluble	85.98	9.52	0.5	0.5	3.26	26	73	1.33
Preasphaltene	83.91	6.03	1.5	4.1	2.90	184	800	0.86
THF Soluble <sup>1</sup>	86.08	9.18	0.62	0.89	3.24	30	106	1.28
THF Insoluble	53.34	3.42	ND <sup>2</sup>	7.1	4.7	ND <sup>2</sup>	ND <sup>2</sup>	0.77

<sup>1</sup> Composition for this fraction determined from compositions of toluene soluble and preasphaltene fractions weighted by the yields of these fractions, as shown in Table II.

<sup>2</sup> ND - not determined

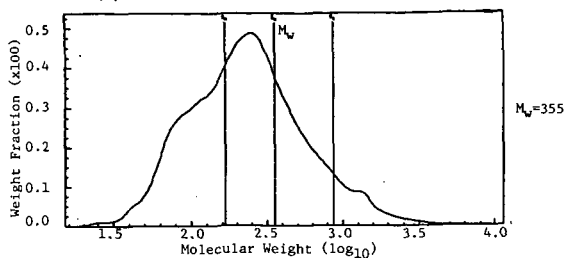
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Figure 1. Schematic of Extraction Procedure

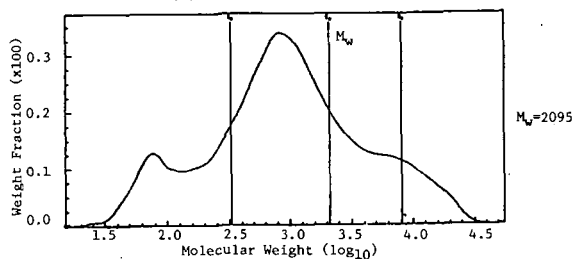


**Figure 2. Molecular Weight Distributions from GPC**  
( $M_w$  = weight-averaged molecular weight)

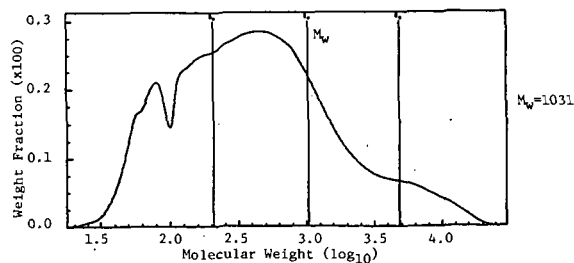
**(a) Toluene Soluble Fraction of Coal Feed**



**(b) 90% Resid/10% DCO Feed**



**(c) Toluene Soluble Fraction of Coprocessing Modified SHFT Solids**



**(d) Preasphaltene Fraction of Coprocessing Modified SHFT Solids**

